Mineralogical composition of genetic horizons of crusty meadow solonetz soil profile from Püspökladány based on X-ray diffraction and thermal analysis

Püspökladányi kérges réti szolonyec szelvény genetikai szintjeinek ásványi összetétele röntgendiffrakciós és termikus analízis alapján

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Abstract – A typical solonetz soil profile, characteristic for the Hortobágy region (Eastern Hungary) was chosen in Ágota-puszta, Püspökladány, to study the mineral distribution in genetic soil horizons. The analyses were carried out for getting data about mineral composition of the region's most typical soil type, and compare it with solonetz profiles from other regions of the Great Hungarian Plain. On the other hands it was aimed to point on the possible mineral transformation processes causing the strong differentiation between genetic horizons of the profile. The analysis established that the mineral composition of the parent rock is very similar to that of other Hungarian solonetz soils. The dominant mineral is quartz (44%). Second frequent mineral group are clay minerals (35%), their proportion is higher than the proportion of the clay size fraction determined by the sedimentation method (19.5%), therefore one part of them falls in the grain-size class >2µm. Main components are also micas (muscovite+illite) (14%) and plagioclase (9%). As a consequence of soil formation, the upper horizons show significant deviation from the mineral composition of the parent rock. In horizon "A" proportion of quartz reaches 59%. A higher amount of clay minerals (45%) is characteristic for the „B" horizon as a result of clay production and illuviation. As final residual products of mineral degradation goethite, hematite, gypsum and amorphous components occur in lesser amounts, without significant differences in their vertical distribution.

Összefoglalás – A Hortobágy területén jellegzetes, tipikus kérges réti szolonyec talajszelvényt választottunk ki Ágota-pusztán arra a célra, hogy a talaj ásványos összetételének genetikai talajszintek közötti különbségeit megvizsgáljuk. A vizsgálatok részben arra irányultak, hogy a vizsgált terület talajait ásványi összetétel tekintetében más hazai szolonyec szelvények adataival összehasonlíthassuk, másrészt pedig az erősen differenciált szolonyec szelvény különböző genetikai szintjei között feltételezhető ásványátalakulások folyamatairól nyerjünk információkat. A vizsgálatok tükrében a talajképző kőzet ásványi összetétele nagyon hasonló más hazai szolonyec talajú területekéhez. Uralkodó ásvány a kvarc (44%). Emellett az agyagásványok jelenléte számottevő (35%), mennyiségük meghaladja az iszapolással meghatározott agyagfrakció mennyiségét (19,5%), tehát egy részük a >2µm nagyságrendbe tartozik. Az alapkőzet jellegzetes ásványai még a csillámok (muszkovit+illit) (14%) és a plagioklászok (9%). A talajképződés következtében kialakult különbségek a szelvényen belül igen jelentősek: a feltalajban („A" szint) a kvarc arányának növekedése (59%), a „B" szintben az agyagosodás és agyagbemosódás következtében megnövekedett agyagásvány-tartalom (45%) jellemző. A talajban zajló mállás termékeinek tekinthető goethit, hematit, gipsz, valamint amorf összetevők kisebb mennyiségben fordultak elő, és eloszlásuk nem mutatott vertikálisan jelentős különbségeket.

Keywords – crusty meadow solonetz, soil minerals, salinization, texture differentiation, soil development
Tárgyszavak – kérges réti szolonyec, talajásványok, szikesedés, szöveti meghatározás, talajfejlődés

Introduction

In respect of their physicochemical properties, horizons of solonetz soil profiles are exceptionally differentiated as a result of their development. This differentiation is expressed also in their different mineral composition. Former publications contain data about mineral composition of solonetz soils from different locations (GEREI-RAKONCZAI 1985, STEFANOVITS 1999, 2003, KUTI et al. 2003), some of them also described mineral transformations (KUTI et al. 2003, SZÉKY-FUX – SZEPESI 1959, SZÖŐR et al. 1991). Our aim was to describe the mineral composition of a profile and to compare it with other solonetz soils of Hungary.

Materials and methods

A meadow solonetz soil profile in Püspökladány (Pl/15; N: 47,342589°; E: 21,077442°) covered with natural short grassland vegetation (*Artemisio-Festucetum pseudovinae*) and semi-vegetated halophytic plant communities (*Camphorosmetum annuae*). The profile was sampled according to genetic horizons. Mineral composition of each horizon was determined by X-ray diffraction and thermal analysis. Genetic horizons were separately sampled, because the description of possible soil mineralogical processes within the profile was aimed. Therefore composition of each horizon was compared with the composition of the "C" horizon (180–200cm depth), which was used as reference, being the supposed parent material of soil forming processes. The last assumption is not completely fulfilled, because the "C" horizon is permanently saturated with water, and therefore modified by its sodium-rich character. But surely this material is less influenced by soil evolution than the "A" and "B" horizons. *Table 1* presents the basic soil data of the horizons. From morphological point of view the profile could be characterized by a very shallow, grayish eluvial „A_{he}" horizon with structureless, loose sandy texture, which material intrudes into the structural cracks of the „B" horizon, and shows solodization characteristics (SZENDREI 1980, 1999). Horizon „B" is a blackish – dark brown, sodic clay and humus accumulation horizon (*Fig.1*), having a columnar structure in 30–35cm depth (B_{tn1}) and a rather prismatic-blocky structure below that (B_{tn2}). From 0 to 80cm there are no carbonates, below that carbonates occur also in form of concretions of size up to 0.5cm. Also other concretions such as limonite, manganese and gley patches are characteristic. Horizon „C_{gk}" is light brownish yellow gleyic infusion loess, with up to 20% clay and 11% carbonate content, patched with iron and manganese oxides and hydroxides. Groundwater level lays mostly deeper than 2m below the surface. The horizon sequence of the profile could be described as A_{eh}-B_{tn}-$B_{tn(k)}$-$C_{g(k)}$ with application of WRB diagnostic soil horizon definitions. The 'k' index in brackets should mean that the carbonate content did not reach the criteria of calcic horizons according to WRB; despite of other, very closely located profiles, which have calcic character in "B" and "C" horizons. The profile could be classified in the Hungarian soil taxonomy (SZABOLCS 1966) as solonchakized crusty meadow solonetz, which is also solodized, but this property does not appear on the level of classification.

genetic horizon	depth of samples (cm)	org.mat. %	pH (H_2O)	pH, (KCl)	$CaCO_3$% (determined with Scheibler-calcimeter)	KA	total salinity %	$NaHCO_3$%	S (mg. eq./100g)	ESP%
A_{eh}	0-5	3.8	7.4	6.9	4.6	38	0.14	0.00	24.4	8.9
B_{tn1}	30-40	1.2	9.0	7.7	4.5	54	0.31	0.07	30.3	45.1
B_{tn2}	60-80	0.8	9.2	7.8	3.3	64	0.39	0.13	28.3	63.0
C_g	180-200	0.5	9.1	7.8	11.0	71	0.27	0.07	39.2	18.4

Table 1 Basic soil data of Pl/15 profile, determined by Hungarian soil laboratory standards

1. táblázat Magyar talajlaboratóriumi szabványok alapján meghatározott alapvető talaj adatok a Pl/15 szelvényben

For the X-ray analysis samples were taken from the horizons listed in *Table 1*. The grain-size fraction >0.1mm was removed by wet sieving. Samples were carefully dried (at ca. 40°C), than homogenized and ground with ceramic mortar and pestle. For thermal analysis samples from horizons „A" (0–5cm), „B" (40–60cm) and „C" (180–200cm) were used. The grain-size fraction <0.002mm was also separately analyzed, it was separated from samples mentioned before by sedimentation technique. Analyses were carried out by Derivatograph-PC instrument, samples were heated in the interval 25 to 1000°C, heating rate: 10°C/min, in platinum crucible. Al_2O_3 preheated at 1500°C was used as reference material. Derivatograms were evaluated by the software of the instrument based on former analyses (PAULIK & PAULIK 1981, SZÖŐR 1982, SZÖŐR et al. 1984, 1991, SZÖŐR & BALÁZS 1988). The amount of KOH-soluble silicate was also determined in each horizon by Gedroiz's method (BALLENEGGER 1962).

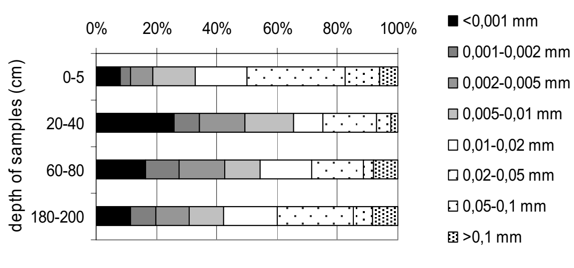

Figure 1 Particle size distribution in the profile Pl/15 determined with sedimentation method

1. ábra Ülepítéses módszerrel meghatározott szemcseméret eloszlási adatok a Pl/15 szelvényben

Results

In each horizon quartz could be determined by X-ray analysis as dominant soil mineral (*Table 2*). On the surface its total amount is higher than below. Enrichment of quartz in the topsoil („A_{eh}" horizon) could be the result of enrichment of primary quartz derived from the sand fraction of the soil because of texture differentiation. SZÉKY-FUX – SZEPESI (1959) reported very similar vertical distribution of quartz in solonetz profiles from Hortobágy. When fine components were leached out and moved downwards by illuviation, the relative proportion of quartz increased in the topsoil.

Mica (muscovite) is present only in the „C" (14%) and B_{tn2} (11%) horizons. Its amount is the highest in the deepest horizon, its transformation into clay minerals in the topsoil (above 60cm) can be supposed. A higher amount of clay minerals and the absence of mica in the topsoil may be the result of this mineral transformation. Because by X-ray analysis differentiation of mica from illite is not always clear, the sum of their amounts is given the tables and diagrams (*Table 2, Fig. 2, Fig. 4*). The content of plagioclases is the lowest in „B_{tn1}" horizon which is the site of the most intense mineral transformation in the profile. Higher amounts of plagioclase and mica in horizon „A_{eh}" can be the result of texture differentiation, in a similar manner as in the case of quartz. According to X-ray analysis amphibole occurs in very small amounts. Calcite is missing from „A_{eh}" and from top of „B_{tn}" while accumulation in lower „B_{tn}" horizon could be established with slightly higher calcite content as in horizon „C". Its vertical distribution is affected by the pH regulating function of CO_3^{2-} content of percolating rainwater, total amount of organic acid and CO_3^{2-} production of the root system, and the Na^+-rich rising groundwater as well. The depth of carbonate accumulation varies with seasonal variation of pH and moisture, which is very typical for this genetic soil type (SZENDREI 1999). Thermal analysis determined also microcrystalline calcite with Mg^{2+}. Carbonate contents of the samples determined by Scheibler calcimeter (*Table 1*) were higher (by almost 2x) than the carbonate contents determined by thermal and X-ray measurements. The difference can be explained by the different preparation of samples for standard soil laboratory (calcimetric) analysis, and for XRD and DTA: samples for calcimeter analysis were untreated (except for homogenization) but for XRD and DTA analyses the fraction above 0.1mm was removed by wet sieving. We suppose that wet sieving washed out a part of the carbonate content from the soil. On the other hand in lower horizons carbonate occurs particularly in the form of concretions, the grain-size of which is over 0.1mm in diameter and they were also removed by sieving.

Amorphous components are present in 3–5%. KOH soluble silicates determined by Gedroiz's method are less than half of the total amorphous material determined by XRD (*Table 3*). The rest of the amorphous components could be other residuals of mineral disintegration (iron and aluminium hydroxides). Differences between horizons in amounts of amorphous silica could be facilitated by its mobility if free Na^+ and K^+ ions are present constituting water soluble „water glass" (sodium and potassium silicates) (SZABOLCS 1954). They rise upwards with capillary water and than precipitate and accumulate on the surface (BAKER & SCRIVNER 1985).

genetic horizon	depth of samples (cm)	montmorillonite	illite/montmorillonite	illite+muscovite	kaolinite	chlorite	quartz	K-feldspar	plagioclase	amphibole	calcite	dolomite	hematite	goethite	gypsum	amorphous
A_{eh}	0–5	10	5	9		2	59	2	8	1			1			3
B_{tn1}	30–40	19	6	15	2	3	40	3	5				2			5
B_{tn2}	60–80	8	9	11		5	43	2	10	1	6	1	1		+	3
C_g	180–200	10	5	14		6	44	2	9		5		1	+		4

Table 2 Mineral composition (%) in genetic horizons of profile Pl/15 determined by the X-ray diffraction analysis

2. táblázat Röntgendiffrakciós elemzéssel meghatározott ásványos alkotók (%) a Pl/15 szelvény genetikus szintjeiben

genetic horizon	depth of samples (cm)	KOH soluble silicates (%)	amorphous by XRD (%)
A_{eh}	0–5	0.95	3
B_{tn1}	30–40	1.71	5
B_{tn2}	60–80	1.03	3
C_g	180–200	0.99	4

Table 3 Amount of KOH soluble silicates determined by Gedroitz's method and amorphous components based on X-ray diffraction analysis in the Pl/15 profile

3. táblázat A KOH-ban oldható szilikátok (Gedroitz módszere szerint) és az amorf összetevők mennyisége röntgendiffrakciós elemzés alapján a Pl/15 szelvényben

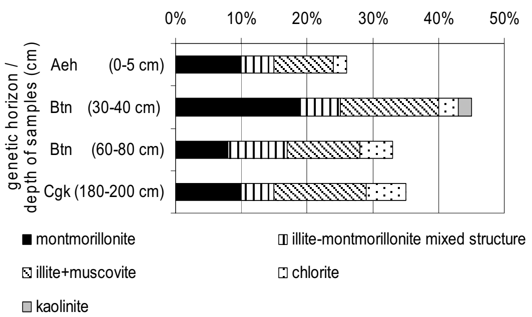

Figure 2 Vertical distribution of clay minerals in the Pl/15 profile based on X-ray diffraction analysis

2. ábra Agyagásványok vertikális eloszlása a Pl/15 szelvényben, röntgendiffrakciós elemzés alapján

Total amount of clay minerals in „B_{tn1}" is more than twice as much, as in the „A" horizon (*Fig. 2*). In horizon „A_{eh}" the proportion of clay minerals determined by XRD (26%) is significantly higher than the proportion of particle size fraction <2μm (11.5%). It means that considerable part of clay minerals in the „A_{eh}" falls in the size fraction >2μm. The same is the case in the upper horizon „B_{tn1}" (clay minerals by XRD: 45%, fraction <2μm: 34.1%) and in the lower horizon „B_{tn2}" (clay minerals: 33%, fraction <2μm: 27.5%) and in horizon „C_g" (clay minerals: 35%, fraction <2μm: 19.5%). In the last case, an unchanged mineral composition of the original sediment can be supposed while in the topsoil there are clay mineral aggregates of particle size >2μm produced by very intense weathering of primary minerals (mostly mica and feldspars). In the same time illuviation of colloidal (<2μm) dissolution residuals (amorphous silicates, iron, and aluminium hydroxides) may explain the higher colloid proportion in the „B" horizon. Among the three-layer clay minerals montmorillonite is dominant, its highest amount is in the B_{tn1} horizon. The amount of illite/montmorillonite mixed-layer clay minerals is lower than that of montmorillonite and shows a maximum in the lower „B_{tn2}" horizon. Illite is missing in „C" and in the lower „B_{tn2}", but as mentioned before its amount is given together with mica because of their problematic differentiation. In the topsoil ("A") its amount is near that of montmorillonite. Chlorite is present in all horizons but everywhere in very small quantity, its amount increases with depth. In the upper „B_{tn1}" horizon also minor kaolinite could be detected. The most intense mineral transformation producing clay minerals can be supposed in the topsoil. The distribution of clay minerals is influenced also by illuviation and accumulation of the colloid particles in the „B" horizon. Low quantities of iron oxides (hematite: Fe_2O_3), and oxy-hydroxides (goethite: $FeO(OH)$), furthermore dolomite ($CaMg(CO_3)_2$) and evaporites like gypsum ($CaSO_4 \cdot 2H_2O$) were found to be final products in decomposition of silicate minerals. No other salt minerals could be detected in the samples without any further treatment, but from salt crusts and powder-like salt efflorescence thenardite (Na_2SO_4), natron ($Na_2CO_3 \cdot 10H_2O$) and trona ($Na_3CO_3(HCO_3) \cdot 2H_2O$) have been identified by X-ray analysis. VAN UFFELEN (2002) described also occurrence of mirabilite ($Na_2SO_4 \cdot 10\ H_2O$) close to our sampling site (at a distance of 5–7km).

The analysis of the derivatograms confirmed, that the dominant structure of the clay minerals is smectite, the subdominant structures are the mixed-layers (probably illite/montmorillonite). The temperature interval of dehydroxilation indicates atypical structures, which can be the result of mineral degradation because of alkalinization (*Fig. 3*). Smectite could be described as Na-montmorillonite in the topsoil and Ca-montmorillonite in the parent rock.

genetic horizon	depth of samples (cm)	clay minerals (%)	carbonates (%)	organic matter (%)
A_{eh}	0-5	21	-	2.19
B_{tn}	40-60	34	2.88	1.43
C_g	180-200	19	2.57	0.81

Table 4 Clay mineral, carbonate and organic contents (%) in genetic horizons of profile Pl/15 determined by thermal analysis

4. táblázat A Pl/15 szelvény genetikai szintjeinek agyagásvány-, karbonát-, és szervesanyag-tartalma a termikus elemzés alapján

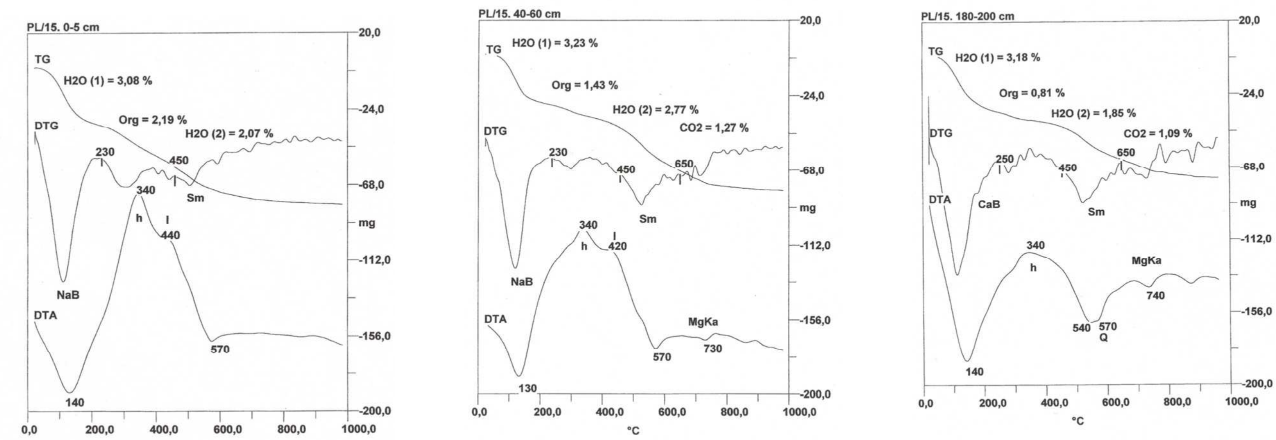

Figure 3 TG, DTG and DTA curves of samples from horizons „A", „B" and „C" of Pl/15 profile.

3. ábra A Pl/15 szelvény "A", "B" és "C" szintjeiből származó minták TG, DTG és DTA görbéi

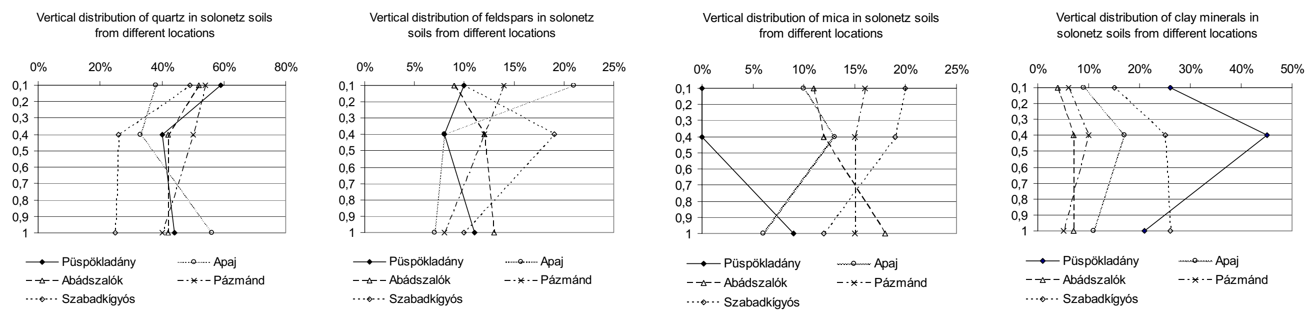

Figure 4 Vertical distribution of mean mineral components in 4 solonetz profiles (GEREI & RAKONCZAI 1985, STEFANOVITS 1999, STEFANOVITS 2003, KUTI et al 2003) and in the profile of Püspökladány (Pl/15) based on X-ray analysis. Vertical scale in metres.

4. ábra Átlagos ásványos összetétel vertikális eloszlása 4 szolonyec szelvényben (GEREI & RAKONCZAI 1985, STEFANOVITS 1999, STEFANOVITS 2003, KUTI et al 2003) és a püspökladányi szelvényben (Pl/15) röntgen elemzés alapján. A függőleges skála mértékegysége méter.

Discusion

As new results in the mineralogy of Hungarian solonetz soils DTA analysis established the presence of Na-montmorillonite in the upper horizons. NEMECZ (2006) points out that it can be an intermediate product of hydrolysis, being between albite and kaolinite. The Na-character of the montmorillonite causes numerous unfavourable physicochemical properties of these soils, and may play important role in regulation of Na content of soil solutions (KUTI et al. 2003).

The distribution of the amount of KOH-soluble silicates showed poor similarity to vertical distribution of the amorphous material indicated by X-ray analysis. Their maximum value could not be measured on the surface – which might have been supposed by physicochemical properties of the „A_{eh}"horizon – but in the „B_{tn}" horizon. Also its value in the „C" horizon was lower than that in the „B_{tn1}" horizon. It suggests intense mineral transformation in the „B" horizon. The very different chemical and physical properties of „A" are rather the final result of the mineral transformation processes active in deeper levels.

Semi-quantitative mineral compositions of other solonetz soils based on X-ray analysis are available from former publications. Data of profiles from Apaj (KUTI et al. 2003), Szabadkígyós (GEREI & RAKONCZAI 1985), Pázmánd (STEFANOVITS 1999), Abádszalók (STEFANOVITS 1999, 2003), Zabszék (KUTI et al. 2003) were compared with our data from Püspökladány (*Fig. 4*). Also KAPOOR et al. (1986) published results on solonetz soils from Hortobágy, but their quantitative data concern only the sand fraction of each horizon, and therefore they are not comparable with our data.

In the profiles compared, the mineral compositions of horizon „C" are only slightly different, however, more significant differences could be observed in the composition of horizons „A" and „B". The solonetz profile from Püspökladány has low feldspar and the highest quartz content in its topsoil as compared to the other profiles, while the feldspar and quartz contents of the „C" horizon do not show significant differences from the parent rock of other profiles. On the other hand, the clay mineral content of the „B" horizons in Püspökladány is seemingly very high in comparison with other profiles. This is partly due, however, to the different definition of the micaceous minerals muscovite and illite. When the sum clay minerals + mica is considered, the difference between the "B" horizons of the Püspökladány and other profiles is much lower.

Although there are differences in mineral composition of soil horizons „A" and „B", the mineral composition of horizon „C" of the Püspökladány profile does not differ significantly from the parent rock of other Hungarian solonetz soils. We have to conclude that at Püspökladány in horizon "B" the soil developing processes produced high amounts of secondary minerals (clay minerals) consequently, lower amounts of primary minerals (feldspars) remained in horizons „A" and „B". The very high quartz content of the topsoil could be the result of texture differentiation: one part of the clay particles produced in the topsoil were leached out from horizon „A" and enriched in „B" while larger quartz particles remained their and became relatively enriched near the surface. This indicates long and intense of mineral differentiation processes in the solonetz soils studied.

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